STRATEGIES FOR SPIROCYCLIC-AMINE SYNTHESIS BASED ON IMINIUM SALT SET-PHOTOCHEMISTRY

ROBERT W. KAVASH and PATRICK S. MARIANO*
Department of Chemistry and Biochemistry University of Maryland
College Park, Maryland 20742, USA

Abstract — Preparative features of photoinduced single electron transfer (SET) reactions of selected N-silylmethallyl-iminium salts have been probed in the context of strategies for functionally complex spirocyclic amine synthesis.

INTRODUCTION

In earlier investigations,[1-4] we have demonstrated that SET-promoted photo-addition and -cyclization reactions between allylsilanes and iminium salts serve as efficient C-C bond forming processes. As depicted in Scheme 1, these excited state reactions proceed *via* pathways involving SET from the allylsilane π-donor to the singlet excited iminium cation, competitive desilylation and radical coupling of the intermediate diradical cation I,[4] and either diradical closure or desilylation of the respective diradical or cation intermediates II and III. Despite the mechanistic complexity of these processes, they often occur with high chemical and quantum efficiencies.

As part of a program designed to develop the synthetic potential of this unique excited state SET process, we have explored the photochemistry of a number of allyl- and benzyl-silane containing iminium salts. As anticipated this N-heterocycle ring forming reaction, exemplified in Scheme 1, does serve as a key element in strategies for the synthesis of selected members of several alkaloid families including the protoberberines[5] and erythrinanes.[6]

A more exacting challenge to the allylsilane-iminium salt photoprocess is found in plans devised for construction of the basic pentacyclic core of members of the cephalotaxus alkaloid family, exemplified by cephalotaxine (1).[7] As shown in
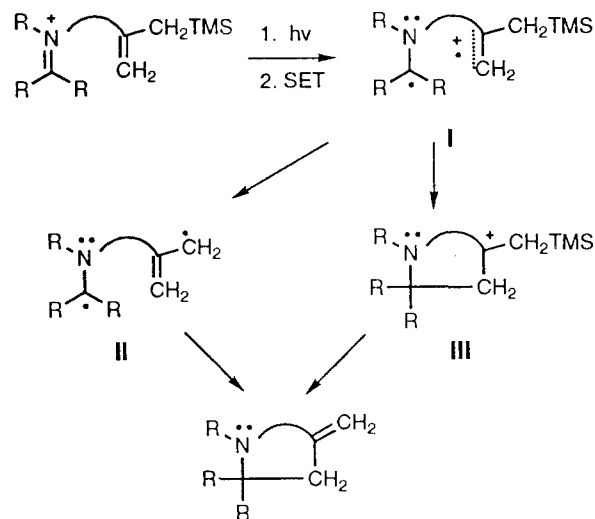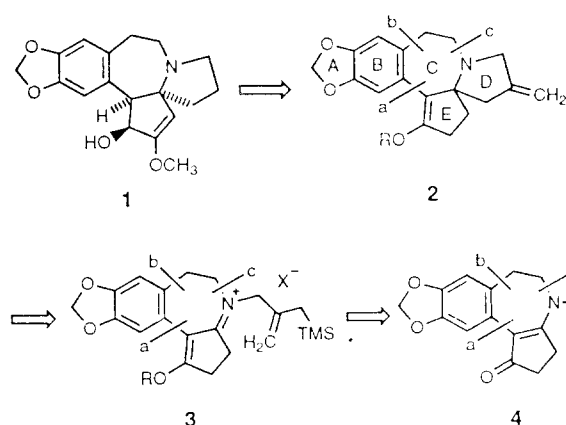

Scheme 1.

Scheme 2, the design incorporates SET-induced photocyclization of iminium salts **3**, derived from β-enamino-ketone precursors **4**, to construct the pyrrolidine element of the target's spirocyclic D-E unit. In the initial generalized strategy, the hydroazepine C-ring would be either present in the photosubstrate or constructed following photocyclization by C-C (bonds a and b in **2**) or C-N (bond c in **2**) bond forming processes.

Observations made in our early exploratory studies in this area[8] indicated that the former approach, employing photocyclization of a C-ring intact iminium salt such as **5**, would be problematic. The

---

* To whom correspondence should be addressed.

Scheme 2.

reason for this is associated with the low excited state reduction potential (*i.e.* more difficulty reduced) of aryl ring conjugated iminium cations which exists in the constrained and, thus, planar C-ring intact systems such as **5**. This prevents efficient SET from the allylsilane donor to the excited iminium cation and, thus, blocks SET-induced photocyclization. In contrast, iminium cations of general structure **6**, which lack an intact hydroazepine C-ring, can possibly exist in non-planar aryl-iminium cation conformation owing to severe steric crowding which could occur in their planar conformers. If so, these systems would behave as simple non-conjugated
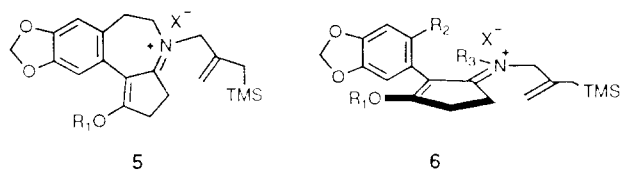
Structures 5-6

iminium salts and, as such, should efficiently participate in intramolecular SET from allylsilane donors in their excited states.

These thoughts suggested that sequences for construction of the cephalotaxine pentacyclic skeleton that relied on photocylization of iminium salts related to **6** followed by installation of the hydroazepine C-ring would be more attractive. As part of a program established to test this proposal and to explore the scope and limitations of the photospirocyclization methodology, we have prepared and subjected to photochemical investigation several structurally complex aryliminium salts. Below, the results of this effort focusing on the synthesis of iminium salts **7-12**, an assessment of their structural properties and an analysis of their photochemical reactivity, are described.
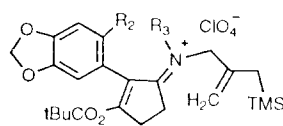
Structures 7-12

MATERIALS AND METHODS

General Procedures. ^{1}H NMR spectra were recorded on IBM WP-200, Bruker AF-200, or Bruker AM-400 spectrometers and chemical shifts (δ) are reported in ppm with either tetramethylsilane or $CHCl_3$ as internal standards. Coupling constants are presented in hertz (Hz) and multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), pd (pentet of doublets), ABq (AB quartet), AA'BB'm (AA'BB' multiplet spin system). ^{13}C NMR spectra were recorded on IBM WP-200 (50 MHz), Bruker AF-200 (50 MHz), or Bruker AM-400 (100 MHz) spectrometers and chemical shifts are reported in ppm relative to $CHCl_3$ as an internal standard. Assignments were made with the aid of an INEPT program. All ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ unless specified otherwise.

Infrared (IR) spectra were recorded on a Perkin-Elmer 298 or a Nicolet 5DXC FT-IR instrument and band positions are expressed in cm^{-1}. Low resolution mass spectra were recorded on a Hitachi RMU-6, an HP 5988A, or a VG 7070E instrument. High resolution measurements were obtained on the VG 7070E or from the Pennsylvania State University Mass Spectrometry Center. Ultraviolet spectra were recorded by use of a GCA McPherson EU-700-56 or a Perkin-Elmer Lambda 5 UV/Visible spectrometer. Melting points were determined with a Griffin Mel-Temp and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

All reported reactions were run under a dried nitrogen atmosphere. Column chromatography was performed with Florisil (100-200 mesh) or Alcoa Type F-20 alumina (neutral, 80-200 mesh). Molecular distillations were achieved with a Kugelrohr apparatus. All products were obtained as oils with purities >90% as judged by NMR analysis unless otherwise specified.

The apparatus employed for preparative irradiations consisted of a N_2-inlet equipped, reaction vessel into which was placed a water-cooled quartz immersion well containing a 450 W Hanovia medium-pressure mercury lamp surrounded by Corex glass filter (5% transmittance at 270 nm, 50% transmittance at 290 nm, 85% transmittance at 310 nm). The progress of each photoreaction was monitored by UV analysis of removed aliquots.

β-Enaminoketone Preparations.3,4-Methylenedioxyphenylacetic acid (16). The synthesis of this known substance was based on a modification of the procedure reported by Semmelhack.[10] A solution of 24.0 g of 86.8% KOH (0.37 mol) in 240 mL of water was added in one portion to a

solution of 19.9 g (0.12 mol) of piperonyl nitrile (15)[10] in 95 mL of ethanol. After stirring at reflux for 6.5 h the mixture was cooled, poured into water, and extracted with CHCl₃. Concentrated HCl was added to the aqueous layer at 4°C to bring the pH to ca. 2. The colorless solid which formed was collected by filtration. Additional material was obtained by ether extraction of the filtrate giving 20.4 g (91%) of the desired acid 16 (mp 128-129°C, lit.[14] mp 128-129°C, from water).

2-(3,4-Methylenedioxyphenyl)ethyl Alcohol (17). The alcohol 17 was prepared by the method of Semmelhack[10] with several modifications. To a solution of 7.80 g (0.20 mol) of 95% LiAlH₄ in 400 mL of THF was slowly added a solution of 29.42 g (0.163 mol) of arylacetic acid 16 in 1 L of THF. The reaction mixture was stirred at 25°C for 2 h and then treated with 8 mL of water, 8 mL of 15% aqueous NaOH solution, and 24 mL of water. The heterogeneous mixture was filtered and the granular precipitate was washed extensively with ether. The filtrate was dried over MgSO₄ and concentrated in vacuo. Molecular distillation (100°C, 0.07 mm) of the crude product mixture gave 24.38 g (90%) of alcohol 17 as a colorless oil whose spectroscopic properties mathched those reported previously.[10]

2-(2-Iodo-4,5-methylenedioxyphenyl)ethyl Alcohol (18). This known compound[10] was prepared by a slight modification of the silver trifluoroacetate mediated iodination procedure of Janssen and Wilson.[11] To a vigorously stirred mixture of 6.35 g (28.7 mmol) of AgO₂CCF₃ and 4.15 (25.0 mmol) of alcohol 17 in 10 mL of CHCl₃ was added slowly 7.30 g (28.7 mmol) of iodine in 375 mL of CHCl₃. After stirring at 25°C for 1.5 h the reaction mixture was filtered and the yellow precipitate was washed extensively with CHCl₃. The filtrate was washed with 10% aqueous Na₂S₂O₃, dried over Na₂SO₄, and concentrated in vacuo giving a brown solid. Recrystallization from methanol-water afforded 6.10 g (83%) of aryl iodide 18 (mp 68.5-69.5°C, lit[10] mp 68-69.5°C).

2-(2-Iodo-4,5-methylenedioxyphenyl)ethyl Methyl Ether (19). To 2.57 g (40.1 mmol) of KOH in 20 mL of DMSO was added 2.93 g (10.0 mmol) of iodoalcohol 18 followed by 1.25 mL (20.1 mmol) of methyl iodide. The resulting mixture was stirred for 1 h at 25°C, poured into water, and extracted with CH₂Cl₂. The organic extracts were washed with water, dried over Na₂SO₄, and concentrated in vacuo to yield 2.98 g (97%) of methyl ether 19 as a colorless solid. Recrystallization from hexanes-ethyl acetate provided pure 19 (mp 69-70.5°C). ¹H NMR 2.93 (t, J=7.0 Hz, 2 H, ArCH₂), 3.36 (s, 3 H, OCH₃), 3.53 (t, J=7.0 Hz, 2 H, CH₂O), 5.94 (s, 2 H, OCH₂O), 6.78 (s, 1 H, ArH), 7.22 (s, 1 H, ArH); ¹³C NMR 40.6 (ArCH₂), 58.5 (OCH₃), 72.1 (CH₂O), 87.9 (C-I aromatic), 101.4 (OCH₂O), 109.9 (C-6), 118.5 (C-3), 134.8 (C-1), 147.0 (C-5), 148.4 (C-4); IR (CHCl₃), 2880, 1500, 1475, 1400, 1380, 1230, 1100, 1040, 940, 860; MS m/z (rel intens) 306 (M, 65), 261 (100), 179 (80), 164 (15), 148 (30), 135 (35), 134 (45); HRMS m/z 305.9733 (C₁₀H₁₁IO₃ requires 305.9753). Anal. Calcd. for C₁₀H₁₁IO₃: C, 39.24; H, 3.62. Found: C, 38.82; H, 3.54.

2-(2-Carboxaldehyde-4,5-methylenedioxyphenyl)ethyl Methyl Ether (20). A solution of 13.23 g (43.2 mmol) of aryliodide 19 in 325 mL anhydrous THF was cooled to -

78°C and 34.6 mL of 1.50 M n-BuLi in hexane (Aldrich) was added. Following addition, the mixture was stirred for 75 min at -78°C. A solution of 10.6 mL (95.4 mmol) of anhydrous N-formylpiperidine (distilled from BaO) in 40 mL anhydrous THF was added and stirring was continued at -78°C for 5.5 h. The cold reaction mixture was poured into an ice water slurry and extracted with CHCl₃. The extracts were combined, washed with water and saturated aqueous NH₄Cl, dried over Na₂SO₄, and concentrated in vacuo to yield an orange oil which was subjected to Florisil column chromatography (90:10 hexanes/ethyl acetate) to yield 7.46 g (82%) of aldehyde 20. ¹H NMR 3.25 (t, J=6.5 Hz, 2 H, ArCH₂), 3.32 (s, 3 H, OCH₃), 3.58 (t, J=6.5 Hz, 2 H, CH₂O), 6.03 (s, 2 H, OCH₂O), 6.76 (s, 1 H, ArH), 7.31 (s, 1 H, ArH), 10.13 (s, 1 H, CHO); ¹³C NMR 32.2 (ArCH₂), 58.5 (OCH₃), 73.3 (CH₂O), 101.8 (OCH₂O), 108.8 (C-6), 110.9 (C-3), 128.9 (C-1), 139.1 (C-2), 146.9 (C-4), 152.1 (C-5), 189.4 (CHO); IR (CHCl₃) 2880, 2720, 1680, 1620, 1610, 1480, 1375, 1260, 1100, 1040, 940, 910; MS m/z (rel intens) 208 (M,85), 177 (15), 176 (90), 175 (20), 163 (75), 148 (100), 147 (30), 135 (45), 77 (45); HRMS m/z 208.0739 (C₁₁H₁₂O₄ requires 208.0736).

2-[2'-(2-Methoxyethyl)-4',5'-methylenedioxyphenyl]-1,3-cyclopentandione (21). To a solution of 7.46 g (35.8 mmol) of aldehyde 20 in 144 mL of anhydrous CH₂Cl₂ cooled to -78°C (dry ice/acetone) was added 4.40 mL (35.8 mmol) of BF₃·OEt₂. After stirring for 20 min a solution of 10.4 g (42.9 mmol) of 95% 1,2-bis(trimethylsilyloxy)cyclobutene (Aldrich) in 72 mL of anhydrous CH₂Cl₂ was added dropwise. The mixture was stirred at -78°C for 7 h, poured into 5% aqueous NaHCO₃, and extracted with ether. The ethereal extracts were dried over Na₂SO₄ and concentrated in vacuo to yield 13.86 g of a residue. A solution of the residue in 80 mL of trifluoroacetic acid at 0°C was sonnicated for 30 min, poured into 400 mL of 0°C methanol and concentrated in vacuo. Crystallization of the residue from ethyl acetate yielded 7.66 g (75%) of 21 (mp 168-169°C). ¹H NMR (CD₃OD) 2.61 (t, J=7.3 Hz, 2 H, ArCH₂), 2.63 (s, 4 H, CH₂-CH₂), 3.27 (s, 3 H, OCH₃), 3.42 (t, J=7.3 Hz, 2 H, CH₂O), 5.90 (s, 2 H, OCH₂O), 6.48 (s, 1 H, ArH), 6.78 (s, 1 H, ArH); ¹³C NMR (CD₃OD) 31.6 (C-4 and C-5, CH₂-CH₂), 34.4 (ArCH₂), 58.6 (OCH₃), 74.4 (CH₂O), 102.2 (OCH₂O), 110.5 (C-3'), 111.7 (C-6'), 119.6 (C-2), 124.6 (C-1'), 133.4 (C-2'), 147.4 (C-4'), 148.8 (C-5'), 198.0 (C-1 and C-3, C=O); IR (KBr) 3600-2300, 2880, 2620, 1665 (weak), 1570 (strong), 1490, 1380, 1310, 1230, 1040, 930, 880, 830; MS, m/z (rel intens) 276 (M, 15), 245 (15), 244 (100), 231 (13), 229 (19), 201 (13), 189 (19), 188 (64), 173 (11), 160 (20), 115 (10); HRMS m/z 276.1009 (C₁₅H₁₆O₅ requires 276.0998). Anal. Calcd. for C₁₅H₁₆O₅: C, 65.21; H, 5.84. Found: C, 64.86; H, 5.79.

3-Chloro-2-[2'-(2-methoxyethyl)-4', 5'-methylenedioxyphenyl]-2-cyclopenten-1-one (22). To a suspension of 6.85 g (24.8 mmol) of 2-aryl-1,3-dione 21 in 50 mL of distilled water was added 92.0 mL of 0.27 M NaOH (24.8 mmol) dropwise. The mixture was stirred for 60 min at 25°C and the water was removed by vacuum distillation to afford 7.46 g (100%) of the sodium salt of 21 (mp 196-200°C). To a solution of this salt in 150 mL of anhydrous benzene at 10°C was added dropwise a solution of 3.50 mL

(40.1 mmol) of oxalyl choride in 50 mL of anhydrous benzene. The resulting reaction mixture was stirred at 50-55°C for 22 h, cooled to 10°C, poured into cold 5% aqueous NaHCO$_3$, and extracted with benzene. The benzene extracts were washed with brine, dried over Na$_2$SO$_4$, and concentrated *in vacuo* to yield 7.28 g (99%) of chloroenone **22**. ^{1}H NMR 2.53-2.63 (p of d, J=7.0, 7.2 Hz, 2 H, ArCH$_2$), 2.67-2.69 (apparent t, J=4.9 Hz, 2 H, CH$_2$-C=O), 2.94-2.97 (d of t, J=4.7 Hz, 5.0 Hz, 2 H, CH$_2$-C=C(Cl)), 3.26 (s, 3 H, OCH$_3$), 3.34-3.44 (m, 2 H, CH$_2$O), 5.90, 5.93 (ABq, J=1.4 Hz, 2 H, OCH$_2$O), 6.47 (s, 1 H, ArH), 6.78 (s, 1 H, ArH); ^{13}C NMR 33.1 (C-5), 33.5 (ArCH$_2$), 35.4 (C-4), 58.4 (OCH$_3$), 73.2 (CH$_2$O), 101.2 (OCH$_2$O), 109.4 (C-3'), 109.8 (C-6'), 122.2 (C-1'), 131.8 (C-2'), 142.2 (C-2), 146.2 (C-4'), 148.2 (C-5'), 165.9 (C-3), 202.7 (C-1, C=O); IR (CHCl$_3$) 2880, 1705, 1630, 1610, 1480, 1370, 1245, 1100, 1040, 940, 910, 860; MS m/z (rel intens) 296, 294 (M+2, 16; P, 48), 264, 262 (25, 75), 251, 249 (17, 51), 236, 234 (39, 92), 227 (100), 209, 207 (33, 100), 199 (45), 185 (100), 172 (65); HRMS m/z 294.0660 (C$_{15}$H$_{15}$ClO$_4$ requires 294.0659).

3-[[2-[(Trimethylsilyl)methyl]-2-propenyl]amino]-2-[2'-(2-methoxyethyl)-4',5'-methylenedioxyphenyl]-2-cyclopenten-1-one (**23**). A two phase solution of 4.25 g (29.6 mmol) of 2-trimethylsilylmethyl-2-propenyl-1-amine,^{15} 7.28 g (24.7 mmol) of chloroenone **22**, and 10.25 g (74.2 mmol) of K$_2$CO$_3$ in 400 mL of 95:5 (v/v) CH$_3$CN/H$_2$O was stirred at 75-80°C for 80 h. The reaction mixture was cooled to 0°C, poured into cold saturated aqueous NaHCO$_3$, extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extracts were dried over Na$_2$SO$_4$ and concentrated *in vacuo* to give a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to yield 8.16 g (82%) of enaminone **23**. UV max (CH$_3$CN) 276 nm (ε 24900); ^{1}H NMR 0.01 (s, 9 H, Si(CH$_3$)$_3$), 1.46 (s, 2H, CH$_2$Si), 2.47-2.52 (m, 2 H, CH$_2$-C=C), 2.60-2.68 (m, 4 H, ArCH$_2$ and CH$_2$-C=O), 3.25 (s, 3H, OCH$_3$), 3.49 (t, J=6.9 Hz, 2 H, CH$_2$O), 3.66 (d, J=6.2 Hz, 2 H, NCH$_2$), 4.65, 4.69 (ABq, J=1.0 Hz, 2 H, C=CH$_2$), 5.54 (br t, J=6.2 Hz, 1 H, N-H), 5.86, 5.91 (ABq, J=1.4 Hz, 2 H, OCH$_2$O), 6.54 (s, 1 H, ArH), 6.79 (s, 1 H, ArH); ^{13}C NMR -1.5 (Si(CH$_3$)$_3$, 24.1 (CH$_2$Si), 24.2 (C-4), 33.1 (C-5), 33.2 (ArCH$_2$), 49.5 (NCH$_2$), 58.5 (OCH$_3$), 73.1 (CH$_2$O), 100.8 (OCH$_2$O), 107.8 (C=CH$_2$), 109.4 (C-3'), 110.6 (C-6'), 113.7 (C-2), 124.3 (C-1'), 132.3 (C-2'), 143.6 (C=CH$_2$), 146.4 (C-4'), 147.4 (C-5'), 173.4 (C-3), 200.6 (C-1, C=O); IR 3400, 2920, 1660 (w), 1640 (w), 1585 (s), 1490, 1465, 1410, 1245, 1110, 1040, 935, 850, 840; MS m/z (rel intens) 401 (M, 3), 386 (9), 369 (31), 242 (100), 228 (16), 135 (16), 91 (13), 73 (67); HRMS m/z 401.1992 (C$_{22}$H$_{31}$SiNO$_4$ requires 401.2022).

3-[[2-[(Trimethylsilyl)methyl]-2-propenyl]amino]-2-(3',4'-methylene-dioxyphenyl)-2-cyclopenten-1-one (**26**). A solution of 395 mg (2.75 mmol) of 2-trimethylsilylmethyl-2-propenyl-1-amine,^{15} 494 mg (2.09 mmol) of the known^5 chloroenone **25** (made starting with piperonal (**13**) via the arylcyclopentandione (**24**)) and 866 mg (6.26 mmol) of K$_2$CO$_3$ in 55 mL of 95:5 (v/v) CH$_3$CN/H$_2$O was stirred at 75-80°C for 60 h. The reaction was cooled to 0°C, poured

into saturated aqueous NaHCO$_3$ and extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extracts were dried over Na$_2$SO$_4$ and concentrated *in vacuo* to give a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to afford 618 mg (86%) of enaminone **26** (mp 119-121°C). UV max (CH$_3$CN) 280 nm (ε 21200); ^{1}H NMR 0.02 (s, 9 H, Si(CH$_3$)$_3$), 1.49 (s, 2H, CH$_2$Si), 2.44-2.63 (AA'B'B'm, 4 H, CH$_2$-CH$_2$), 3.70 (d, J=6.5 Hz, 2 H, N-CH$_2$), 4.67, 4.72 (ABq, J=0.9 Hz, 2H, C=CH$_2$), 5.69 (br t, J=6.5 Hz, 1 H, N-H), 5.91 (s, 2 H, OCH$_2$O), 6.72-6.86 (m, 3 H, aromatic H's); ^{13}C NMR -1.5 (Si(CH$_3$)$_3$), 23.9 (CH$_2$Si), 24.2 (C-4), 33.0 (C-5), 49.4 (NCH$_2$), 100.7 (OCH$_2$O), 107.8 (C=CH$_2$), 108.6 (C-5'), 109.3 (C-2'), 113.0 (C-2), 121.5 (C-6'), 126.0 (C-1'), 143.5 (C=CH$_2$), 146.0 (C-4'), 147.9 (C-3'), 172.6 (C-3), 200.3 (C-1, C=O); IR (CHCl$_3$) 3400, 3020, 2960, 2900, 1650, 1630, 1590, 1500, 1460, 1410, 1310, 1235, 1090, 1040, 930, 860, 840; MS m/z (rel intens) 343 (M, 23), 328 (5), 270 (7), 187 (7), 149 (26), 85 (100), 73 (81); HRMS m/z 343.1602 (C$_{19}$H$_{25}$SiNO$_3$ requires 343.1604). Anal. Calcd. for C$_{19}$H$_{25}$SiNO$_3$: C, 66.44; H, 7.33; N, 4.08. Found: C, 66.35; H, 7.35; N, 4.09.

3-[Methyl-[2-[(trimethylsilyl)methyl]-2-propenyl]amino]-2-[2'-(2-meth-oxyethyl)-4',5'-methylenedioxyphenyl]-2-cyclopenten-1-one (**27**). A solution of 178 mg (0.443 mmol) of enaminone **23** in 24 mL of anhydrous THF was added to 35 mg (0.88 mmol) of 60% NaH and the resulting mixture was heated at reflux for 60 min. The mixture was cooled to 0°C and 0.28 mL (4.5 mmol) of methyl iodide were added. The reaction was stirred at 25°C for 1 h, cooled to 0°C, poured into water, and extracted with CHCl$_3$ and ethyl acetate. The organic extracts were combined, dried over Na$_2$SO$_4$, and concentrated *in vacuo* to give a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to yield 166 mg (90%) of enaminone **27**. UV max (CH$_3$CN) 282 nm (ε 27600); ^{1}H NMR -0.10 (br s, 9 H, Si(CH$_3$)$_3$), 1.86 (br s, 2 H, CH$_2$Si), 2.43-2.48 (m, 2 H, CH$_2$-C=C), 2.65-2.68 (m, 7 H, ArCH$_2$, CH$_2$-C=O, and N-CH$_3$), 3.26 (s, 3 H, OCH$_3$), 3.44 (t, J=7.4 Hz, 2 H, CH$_2$O), 3.66 (br s, 2 H, NCH$_2$), 4.60, 4.69 (br s and br s, 2 H, C=CH$_2$), 5.85, 5.89 (ABq, J=1.4 Hz, 2 H, OCH$_2$O), 6.51 (s, 1 H, ArH), 6.72 (s, 1 H, ArH); ^{13}C NMR -1.4 (Si(CH$_3$)$_3$), 24.1 (CH$_2$Si), 27.3 (C-4), 33.0 (C-5), 33.8 (ArCH$_2$), 39.5 (N-CH$_3$), 58.4 (OCH$_3$), 58.8 (NCH$_2$), 73.1 (CH$_2$O), 100.8 (OCH$_2$O), 107.5 (C=CH$_2$), 109.2 (C-3'), 111.6 (C-6'), 113.2 (C-2), 128.0 (C-1'), 132.3 (C-2'), 141.2 (C=CH$_2$), 145.6 (C-4'), 147.0 (C-5'), 171.6 (C-3), 202.1 (C-1, C=O); IR (CHCl$_3$) 2920, 1655, 1640, 1565 (s), 1500, 1490, 1470, 1405, 1360, 1310, 1250, 1110, 1040, 940, 855, 840; MS m/z (rel intens) 415 (M, 10), 400 (20), 384 (22), 383 (46), 368 (10), 355 (7), 310 (16), 256 (100), 242 (44), 228 (14), 185 (11), 84 (50), 73 (53); HRMS m/z 415.2199 (C$_{23}$H$_{33}$SiNO$_4$ requires 415.2178).

3-[Methyl-[2-[(trimethylsilyl)methyl]-2-propenyl]amino]-2-(3',4'-methyl-ene-dioxyphenyl)-2-cyclopenten-1-one (**28**). A solution of 145 mg (0.422 mmol) of enaminone **26** in 25 mL of anhydrous THF was added to 34 mg (0.85 mmol) of 60% NaH and the resulting mixture was heated at reflux for 60 min. The mixture was cooled to 0oC and 0.27 mL (4.3 mmol) of methyl iodide were added. The reaction was

stirred at 25°C for 16 h, cooled to 0°C, poured into water, and extracted with CHCl₃ and ethyl acetate. The organic extracts were combined, dried over Na₂SO₄, and concentrated in vacuo giving a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to afford 124 mg (82%) of enaminone **28**. UV max (CH₃CN) 283 nm (ε 22700); ¹H NMR -0.02 (s, 9 H, Si(CH₃)₃), 1.33 (s, 2 H, CH₂Si), 2.42-2.64 (AA'BB'm, 4 H, CH₂-CH₂), 2.73 (s, 3 H, N-CH₃), 3.64 (s, 2 H, NCH₂), 4.61, 4.69 (ABq, J=1.0 Hz, 2 H, C=CH₂), 5.88 (s, 2 H, OCH₂O), 6.57 (dd, J=7.9, 1.6 Hz, 1 H, H-6' aromatic), 6.63 (d, J=1.2 Hz, 1 H, H-2' aromatic), 6.73 (d, J=7.9 Hz, 1 H, H-5' aromatic); ¹³C NMR -1.4 (Si(CH₃)₃), 24.0 (CH₂Si), 27.3 (C-4), 33.1 (C-5), 40.2 (N-CH₃), 59.1 (NCH₂), 100.8 (OCH₂O), 107.7 (C=CH₂), 107.9 (C-5'), 111.4 (C-2'), 114.3 (C-2), 124.2 (C-6'), 128.9 (C-1'), 141.5 (C=CH₂), 146.4 (C-4'), 147.2 (C-3'), 171.6 (C-3), 202.2 (C-1, C=O); IR (CHCl₃) 2940, 1660, 1640, 1565 (s), 1490, 1405, 1310, 1230, 1035, 935, 900, 850 835; MS m/z (rel intens) 357 (M, 68), 342 (14), 284 (100), 244 (15), 242 (16), 230 (15), 188 (53), 73 (79); HRMS m/z 357.1761 (C₂₀H₂₇SiNO₃ requires 357.1761).

3-[Benzyl[-2-[(trimethylsilyl)methyl]-2-propenyl]amino]-2-[2'-(2-methoxy-ethyl)-4',5'-methylenedioxyphenyl]-2-cyclopenten-1-one (**29**). A solution of 821 mg (2.04 mmol) of enaminone **23** in 80 mL of anhydrous THF was added to 122 mg (3.05 mmol) of 60% NaH and the resulting mixture was heated at reflux for 60 min. The mixture was cooled in an ice bath and a solution of 0.61 mL (5.2 mmol) of benzyl bromide (distilled from CaH₂) in 40 mL of anhydrous THF was added dropwise. The reaction was stirred at 25°C for 60 h, cooled to 0°C, poured into ice water, and extracted with ether. The ethereal layers were combined, dried over Na₂SO₄, and concentrated in vacuo to yield a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to afford 868 mg (86%) of enaminone **29**. UV max (CH₃CN) 282 nm (ε 31600); ¹H NMR -0.06 (br s, 9 H, Si(CH₃)₃), 1.39 (br s, 2 H, CH₂Si), 2.48-2.53 and 2.77-2.82 (AA'BB'm, 4 H, CH₂-CH₂), 2.60-2.66 (br m, 2 H, ArCH₂), 3.25 (s, 3 H, OCH₃), 3.40-3.47 (br m, 2 H, CH₂O), 3.64 (br s, 2 H, NCH₂), 4.30 (br s, 2 H, ArCH₂N), 4.73 (br s, 2 H, C=CH₂), 5.81, 5.82 (br s and br s, 2 H, OCH₂O), 6.37 (br s, 1 H, ArH), 6.67 (br s, 1 H, ArH), 6.91 (br s, 2 H, benzyl group ArH), 7.25 (br s, 3 H, benzyl group ArH); ¹³C NMR -1.5 (Si(CH₃)₃), 24.1 (CH₂Si), 27.5 (C-4), 32.8 (C-5), 33.7 (ArCH₂), 53.3 (NCH₂), 55.6 (ArCH₂N), 58.4 (OCH₃), 73.2 (OCH₂), 100.7 (OCH₂O), 107.2 (C=CH₂), 109.3 (C-3'), 111.2 (C-6'), 113.6 (C-2), 126.4 (benzyl group C-H aromatic), 127.3 (C-1'), 127.5, 128.7 (benzyl group C-H aromatic), 132.1 (C-2'), 136.7 (benzyl group C-1 aromatic), 141.3 (C=CH₂), 145.6 (C-4'), 147.1 (C-5'), 171.6 (C-3), 202.7 (C-1, C=O); IR (CHCl₃) 2980, 2950, 2880, 1650, 1560, 1480, 1460, 1430, 1355, 1300, 1240, 1150, 1100, 1035, 935, 880, 850, 835, 690; MS m/z (rel inten) 491 (M, 4), 476 (10), 459 (23), 418 (8), 386 (6), 368 (31), 332 (20), 242 (7), 228 (11), 91 (50), 84 (100), 73 (46); HRMS m/z 491.2483 (C₂₉H₃₇SiNO₄ requires 491.2492).

3-[Benzyl-[2-[(trimethylsilyl)methyl]-2-propenyl]amino]-2-(3',4'-methyl-enedioxyphenyl)-2-cyclopenten-1-one (**30**).

A solution of 306 mg (0.891 mmol) of N-H enaminone **26** in 40 mL of anhydrous THF was added to 70 mg (1.75 mmol) of 60 % NaH and the resulting mixture was heated at 60-65°C for 2 h. The mixture was cooled to 0oC and a solution of 0.43 mL (3.6 mmol) of benzyl bromide (distilled from CaH₂) in 32 mL of anhydrous THF was added dropwise. The reaction was stirred at 25°C for 80 h, cooled to 0°C, poured into ice water, and extracted with ether. The ethereal layers were combined, dried over Na₂SO₄, and concentrated in vacuo to yield a residue which was subjected to Florisil column chromatography (50:50 hexanes/ethyl acetate) to afford 214 mg (55%) of enaminone **30**. UV max (CH₃CN) 282 nm (ε 24300); ¹H NMR -0.08 (s, 9 H, Si(CH₃)₃), 1.29 (br s, 2 H, CH₂Si), 2.48-2.78 (AA'BB'm, 4 H, CH₂-CH₂), 3.60 (s, 2 H, NCH₂), 4.38 (s, 2 H, ArCH₂N), 4.71, 4.74 (s and s, 2 H, C=CH₂), 5.87 (s, 2 H, OCH₂O), 6.52-6.69 (m, 3 H, H-2', H-5', H-6' aromatic), 6.99-7.02 (br d, J=5.3 Hz, 2H, benzyl group Ar-H), 7.26-7.30 (m, 3 H, benzyl group Ar-H); ¹³C NMR -1.5 (Si(CH₃)₃), 24.0 (CH₂Si), 27.5 (C-4), 32.9 (C-5), 53.5 (NCH₂), 56.0 (ArCH₂N), 100.7 (OCH₂O), 107.7 (C=CH₂), 108.0 (C-5'), 111.2 (C-2'), 114.7 (C-2), 123.9 (C-6'), 126.5, 127.5 (benzyl group C-H aromatic), 128.4 (C-1'), 128.7 (benzyl group C-H aromatic), 136.8 (benzyl group C-1 aromatic), 141.5 (C=CH₂), 146.5 (C-4'), 147.2 (C-3'), 171.6 (C-3), 202.8 (C-1, C=O); IR (CHCl₃) 2980, 2940, 1645, 1560, 1490, 1435, 1330, 1300, 1230, 1210, 1155, 1090, 1035, 935, 880, 850, 835, 690; MS m/z (rel intens) 433 (M, 22), 418 (10), 360 (66), 342 (19), 306 (21), 258 (20), 228 (13), 91 (100), 73 (93); HRMS m/z 433.2072 (C₂₆H₃₁SiNO₃ requires 433.2073).

Iminium Perchlorate Preparations.

N-[3-(Pivaloyloxy)-2-[2'-(2-methoxyethyl)-4',5'-methylenedioxyphenyl] cyclopent-2-enylidene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**7**). A solution of 101 mg (0.253 mmol) of enaminone **23** in 20 mL of anhydrous CH₃CN was cooled to 0°C and 6.00 mL of a freshly prepared 4.22 x10⁻² M solution of anhydrous AgClO₄ (0.253 mmol) in anhydrous CH₃CN were added in one portion. To this mixture at 0°C was slowly added a solution of 0.035 mL (0.28 mmol) of pivaloyl chloride in 30 mL of anhydrous CH₃CN. The reaction was stirred at 0°C for 2 h, warmed to 25°C for 45 min, and filtered through Celite. The filtrate was concentrated in vacuo given a residue which was carefully washed with petroleum ether/ether to yield 146 mg (98%) of iminium salt **7**. UV max (CH₃CN) 277 nm (ε 15800), 241 (ε 12300); ¹H NMR 0.01 (s, 9 H, Si(CH₃)₃), 1.12 (s, 9 H, C(CH₃)₃), 1.51 (s, 2 H, CH₂Si), 2.53-2.81 (m, 2 H, ArCH₂), 3.22 (s, 3 H, OCH₃), 3.27-3.48 (m, 4 H, CH₂-CH₂), 3.56 (p, J=4.8 Hz, 1 H, CHOCH₃), 3.68-3.77 (m, 1 H, CHOCH₃), 4.14, 4.17 (s and s, 2 H, NCH₂), 4.65, 4.74 (s and s, 2 H, C=CH₂), 5.93, 5.96 (ABq, J=1.2 Hz, 2 H, OCH₂O), 6.60 (s, 1 H, ArH), 6.81 (s, 1 H, ArH), 9.70 (br s, 1 H, NH); ¹³C NMR -1.5 (Si(CH₃)₃), 24.6 (CH₂Si), 26.6 (C(CH₃)₃), 28.1 (C-4), 30.8 (C-5), 32.7 (ArCH₂), 39.8 (C(CH₃)₃), 53.4 (NCH₂), 59.0 (OCH₃), 72.6 (CH₂O), 101.6 (OCH₂O), 108.8 (C-3'), 110.0 (C-6'), 110.3 (C=CH₂), 117.9 (C-2), 124.1 (C-1'), 133.0 (C-2'), 139.8 (C=CH₂),

147.0 (C-4'), 149.7 (C-5'), 173.0 (O=C-O), 182.9 (C-3), 190.2 (C-1); IR (CHCl) 3200, 2950, 2900, 1785, 1660, 1590, 1500, 1480, 1380, 1350, 1250, 1150, 1080, 1015, 945, 900, 845; MS m/z (rel intens) 485 (M-HClO$_4$, 4) 454 (4), 401 (4), 400 (5), 385 (8), 384 (14), 369 (23), 279 (4), 242 (76), 28 (17), 149 (22), 147 (31), 73 (70), 57 (100); HRMS m/z 485.2573 (C$_{25}$H$_{39}$SiNO$_5$ requires 485.2598).

N-Methyl-N-[3-(pivaloyloxy)-2-[2'-(2-methoxyethyl)-4',5'-methylene-dioxyphenyl]cyclopent-2-enylidene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**8**). Enaminone **27** (51 mg, 0.12 mmol) was reacted with AgClO$_4$ (0.12 mmol) and pivaloyl chloride (0.14 mmol) under the conditions described for preparation of **7** to afford 72 mg (98%) of iminium salt **8**. UV max (CH$_3$CN) 283 nm (ε 26000); ^{1}H NMR -0.12, 0.05 (s, 9 H, Si(CH$_3$)$_3$), 1.04, 1.06 (s, 9 H, C(CH$_3$)$_3$), 1.05, 1.53 (s, 2 H, CH$_2$Si), 2.48-2.67 (m, 2 H, ArCH$_2$), 3.04-3.59 [m overlapping s, 12 H, m is CH$_2$-CH$_2$ and CH$_2$O; 3.10, 3.48 (s, NCH$_3$), 3.19, 3.24 (s, OCH$_3$)], [3.80 and 4.41 (ABq, J=17.3 Hz), 4.03 and 4.12 (ABq, J=8.3 Hz), 2 H, NCH$_2$], 4.59 and 4.79, 4.63 and 4.82 (s and s, 2 H, C=CH$_2$), 5.91 and 5.96, 5.96 and 5.99 (overlapping ABqs, J=1.3 Hz and J=1.2 Hz, 2 H, OCH$_2$O), 6.65 and 6.82, 6.78 and 6.89 (s and s, 2 H, ArH); ^{13}C NMR -1.7, -1.5 (Si(CH$_3$)$_3$), 24.3, 24.8 (CH$_2$-Si), 26.4 (C(CH$_3$)$_3$), 30.0 (C-4), 31.1, 32.1 (C-5), 33.3 (ArCH$_2$), 39.7 (C(CH$_3$)$_3$), 42.3, 43.7 (NCH$_2$), 58.5 (OCH$_3$), 60.3, 63.6 (NCH$_3$), 72.4, 72.8 (CH$_2$O), 101.4, 101.5 (OCH$_2$O), 108.2, 110.1 (C=CH$_2$), 109.0, 109.6 (C-3'), 109.7, 109.9 (C-6'), 121.2, 121.7 (C-2), 123.0, 123.4 (C-1'), 132.4, 133.0 (C-2'), 138.0, 138.9 (C=CH$_2$), 146.2, 146.7 (C-4'), 148.8, 149.0 (C-5'), 172.8, 172.9 (O=C-O), 184.3, 184.9 (C-3), 185.8, 186.7 (C-1); IR (CHCl) 2920, 2880, 1785, 1640, 1580, 1480, 1380, 1350, 1245, 1150, 1080, 1000, 935, 850, 840; MS m/z (rel intens) 499 (M-HClO$_4$,0.46), 415 (5), 400 (10), 383 (25), 342 (6), 310 (11), 282 (7), 270 (9), 256 (56), 242 (31), 147 (18), 85 (18), 73 (89), 57 (100); HRMS m/z 499.2785 (C$_{26}$H$_{41}$SiNO$_5$ requires 499.2754).

N-Benzyl-N-[3-(pivaloyloxy)-2-[2'-(2-methoxyethyl)-4',5'-methylene-dioxyphenyl]cyclopent-2-enylidene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**9**). Enaminone **29** (493 mg, 1.00 mmol) was reacted with AgClO$_4$ (1.00 mmol) and pivaloyl chloride (1.10 mmol) under the conditions described for preparation of **7** to afford 661 mg (97%) of iminium salt **9** as a 1:1 mixture of E and Z isomers. UV max (CH$_3$CN) 285 nm (ε 27000); ^{1}H NMR -0.22, -0.06 (s, 9 H, Si(CH$_3$)$_3$), 0.85, 1.45 (s, 2 H, CH$_2$Si), 1.04, 1.05 (s, 9 H, C(CH$_3$)$_3$), 2.53-2.64 (m, 2 H, ArCH$_2$), 3.09, 3.22 (s, 3 H, OCH$_3$), 3.15-3.52 (m, 6 H, CH$_2$-CH$_2$ and CH$_2$O), [3.81 and 4.20 (ABq, J=17.0 Hz), 3.92 and 4.29 (ABq, J=18.0 Hz), 2 H, NCH$_2$], [4.31 and 5.03 (ABq, J=15.7 Hz), 4.74 and 5.21 (ABq, J=15.9 Hz), 2 H, ArCH$_2$N], 4.64 and 4.91, 4.81 and 4.95 (s and s, 2 H, C=CH$_2$), [5.77 and 5.87 (ABq, J=1.2 Hz), 5.89 and 5.95 (ABq, J=1.1 Hz), 2H, OCH$_2$O], 6.65 and 6.74, 6.69 and 6.79 (s and s, 2H, H-3' and H-6' aromatic), 7.11 (d, J=6.6 Hz, 1 H, benzyl group ArH), 7.22-7.40 (m, 4H benzyl group ArH); ^{13}C NMR -1.8, -1.6 (Si(CH$_3$)$_3$), 24.4, 24.9 (CH$_2$Si), 26.3 (C(CH$_3$)$_3$), 30.3 (C-4), 31.7, 32.1 (C-5), 33.3

(ArCH$_2$), 39.8 (C(CH$_3$)$_3$), 56.3, 57.3 (NCH$_3$), 58.5, 58.6 (OCH$_3$), 58.7, 59.5 (ArCH$_2$N), 72.7, 72.7 (CH$_2$O), 101.4, 101.4 (OCH$_2$O), 107.7, 110.9 (C=CH$_2$), 109.0, 109.1 (C-3'), 109.7, 109.8 (C-6'), 121.3 (C-2), 122.6, 122.7 (C-1'), 127.2, 127.5, 128.6, 129.0, 129.2, 129.5 (benzyl group C-H aromatic), 131.5, 131.7 (benzyl group C-1 aromatic), 132.1, 132.7 (C-2'), 138.0, 138.3 (C=CH$_2$), 146.1, 146.5 (C-4'), 148.9, 148.9 (C-5'), 172.6, 172.7 (C=C-O), 187.2 (C-3), 187.5, 188.1 (C-1); IR (CHCl) 2980, 2950, 2880, 1785, 1640 (w), 1620 (w), 1565, 1500, 1480, 1445, 1380, 1350, 1245, 1210, 1080, 1040, 1015, 935, 850, 835, 690, 620; MS m/z (rel intens) 576 (M-ClO$_4$, 0.31), 543 (1), 491 (5), 476 (6), 459 (15), 418 (8), 387 (12), 368 (18), 332 (19), 279 (23), 227 (35), 185 (24), 167 (50), 147 (100), 91 (100), 73 (100), 57 (100); HRMS m/z 576.3190 (C$_{31}$H$_{46}$SiNO$_5$ requires 576.3145).

N-Methyl-N-[3-(pivaloyloxy)-2-(3',4'-methylenedioxyphenyl)cyclopen-2-enylidene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**10**). Enaminone **28** (114 mg, 0.32 mmol) was reacted with AgClO$_4$ (0.32 mmol) and pivaloyl chloride (0.36 mmol) under the conditions described for preparation of **7** to afford 172 mg (99%) of iminium salt **10** as a 1:1 mixture of E and Z isomers. UV max (CH$_3$CN) 278 nm (ε 21100); ^{1}H NMR -0.12, 0.04 (s, 9 H, Si(CH$_3$)$_3$), 1.03, 1.08 (s, 9 H, C(CH$_3$)$_3$), 1.03, 1.52 (s, 2 H, CH$_2$Si), 3.06, 3.44 (s, 3 H, NCH$_3$), 3.20-3.40 (m, 4 H, CH$_2$-CH$_2$), 3.95, 4.20 (s, 2 H, NCH$_2$), 4.57 and 4.64, 4.80 (s and s, s 2 H, C=CH$_2$), 5.93 and 5.96, 6.00 (ABq, J=1.1 Hz and s, 2 H, OCH$_2$O), 6.70-6.87 (m, 3 H, aromatic H's); ^{13}C NMR -1.7, -1.5 (Si(CH$_3$)$_3$), 24.2, 24.4 (CH$_2$Si), 26.4 (C(CH$_3$)$_3$), 30.1, 30.2 (C-4), 31.1, 31.9 (C-5), 39.7, 39.8 (C(CH$_3$)$_3$), 42.7, 43.5 (NCH$_2$), 60.8, 63.5 (NCH$_3$), 101.4, 101.5 (OCH$_2$O), 108.6, 109.0 (C-5'), 108.7, 109.9 (C=CH$_2$), 110.0 (C-2'), 122.4, 122.7 (C-2), 123.5, 123.7 (C-6'), 124.0 (C-1'), 137.9, 139.0 (C=CH$_2$), 147.7, 148.1 (C-4'), 148.3, 148.4 (C-3'), 172.8, 172.9 (O=C-O), 184.5, 184.6 (C-3), 185.7, 186.4 (C-1); IR (CHCl) 3025, 2980, 2960, 2910, 1785, 1650, 1590, 1505, 1490, 1440, 1375, 1245, 1160, 1090, 940, 860, 840; MS m/z (rel intens) 441 (M-HClO$_4$, 0.2), 285 (6), 200 (11), 188 (26), 172 (10), 133 (21), 115 (26), 89 (19), 73 (79), 57 (100); HRMS m/z 441.2332 (C$_{23}$H$_{35}$SiNO$_5$ requires 441.2335).

N-Benzyl-N-[3-(pivaloyloxy)-2-(3',4'-methylenedioxyphenyl)cyclopent-2-enylidene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**11**). Enaminone **30** (79 mg, 0.18 mmol) was reacted with AgClO$_4$ (0.18 mmol) and pivaloyl chloride (0.20 mmol) under the conditions described for preparation of **7** to afford 110 mg (97%) of iminium salt **11** as a 1:1 mixture of E and Z isomers. UV max (CH$_3$CN) 287 nm (ε 25100); ^{1}H NMR -0.23, -0.06 (s, 9 H, Si(CH$_3$)$_3$), 0.91 and 0.93, 1.45 (s and s, s, 2H, CH$_2$Si), 1.05, 1.06 (s, 9H, C(CH$_3$)$_3$), 3.47-3.55 (m, 4 H, CH$_2$-CH$_2$), 3.83, 4.08 (br s, s, 2 H, NCH$_2$), 4.61 and 4.68, 4.70 and 4.84 (s and s, 2H, C=CH$_2$), 4.81, 4.95 (s, 2 H, ArCH$_2$N), 5.87 and 5.97, 5.93 (ABq, J=1.1 Hz and s, 2 H, OCH$_2$O), 6.66-6.79 (m, 3 H, H-2', H-5', H-6' aromatic), 7.10 (d, J=6.3 Hz, 1 H, benzyl group ArH), 7.26-7.40 (m, 4 H, benzyl group ArH); ^{13}C NMR -1.8, -1.6 (Si(CH$_3$)$_3$), 24.3, 24.5 (CH$_2$Si), 26.3 (C(CH$_3$)$_3$), 30.3, 30.4 (C-4), 31.7, 32.1 (C-5), 39.7, 39.7 (C(CH$_3$)$_3$), 56.4, 57.2 (NCH$_3$), 58.8, 59.6

(ArCH₂N), 101.4, 101.6 (OCH₂O), 108.5, 110.5 (C=CH₂), 108.6, 108.9 (C-5'), 109.7, 110.1 (C-2'), 122.3, 122.4 (C-2), 123.3, 123.6 (C-1'), 123.4, 123.7 (C-6'), 127.3, 128.1, 128.5, 128.9, 129.1, 129.4 (benzyl group C-H aromatic), 131.3, 131.8 (benzyl group C-1 aromatic), 137.8, 138.7 (C=CH₂), 147.6, 148.0 (C-4'), 148.2, 148.3 (C-3'), 172.6, 172.6 (O=C-O), 187.2, 187.2 (C-3), 187.4, 187.7 (C-1); IR (CHCl₃) 2980, 2950, 2890, 1785, 1640 (w), 1565, 1480, 1440, 1350, 1230, 1080, 1015, 930, 850, 840, 690, 620; MS m/z (rel intens) 517 (M-HClO₄, 0.33), 433 (13), 360 (15), 149 (16), 147 (30), 91 (47), 85 (100), 75 (27), 73 (74), 57 (100); HRMS m/z 517.2666 (C₃₁H₃₉SiNO₄ requires 517.2648).

N-[3-(Pivaloyloxy)-2-(3',4'-methylenedioxyphenyl) cyclopent-2-enylid-ene]-N-[2-[(trimethylsilyl)methyl]-2-propenyl]ammonium Perchlorate (**12**). Enaminone **26** (47 mg, 0.14 mmol) was reacted with AgClO₄ (0.14 mmol) and pivaloyl chloride (0.15 mmol) under the conditions described for preparation of **7** to afford 69 mg (95 %) of iminium salt **12** as a 1:1 mixture of E and Z isomers. UV max (CH₃CN) 269 nm (ε 17800); ¹H NMR 0.03 (s, 9 H, Si(CH₃)₃), 1.19 (s, 9 H, C(CH₃)₃), 1.54 (s, 2 H, CH₂Si), 3.24-3.44 (AA'BB'm, 4 H, CH₂-CH₂), 4.18, 4.21 (s and s, 2 H, NCH₂), 4.71, 4.77 (s and s, 2 H, C=CH₂), 5.98 (s, 2 H, OCH₂O), 6.78-6.94 (m, 3 H, aromatic H's), 9.19 (br s, 1 H, NH); ¹³C NMR -1.6 (Si(CH₃)₃), 24.5 (CH₂Si), 26.6 (C(CH₃)₃), 28.1 (C-4), 30.8 (C-5), 39.9 (C(CH₃)₃), 53.3 (NCH₂), 101.6 (OCH₂O), 109.2 (C-5'), 109.4 (C-2'), 110.5 (C=CH₂), 118.5 (C-2), 123.1 (C-6'), 123.9 (C-1'), 139.8 (C=CH₂), 148.8 (C-4'), 149.1 (C-3'), 173.0 (O=C-O), 181.3 (C-3), 190.2 (C-1); IR (CHCl₃) 3200, 3020, 2980, 2960, 1780, 1655, 1600, 1500, 1490, 1380, 1345, 1245, 1210, 1090, 1050, 1020, 930, 845; MS m/z (rel intens) 427 (M-HClO₄, 1.5), 343 (9), 270 (7), 149 (8), 147 (8), 91 (6), 85 (29), 73 (38), 57 (100); HRMS m/z 427.2151 (C₂₄H₃₃SiNO₄ requires 427.2179).

Photochemical Reactions.

General Procedure for the Irradiation of Iminium Salts. Solutions of the iminium salts in CH₃CN were prepared in the concentration range of 0.5 to 3.5 x 10⁻³ M. The solutions were purged with nitrogen and irradiated with Corex filtered-light until the absorbances at the UV λ_max for the iminium salt were 45 to 50% of the initial values. Saturated aqueous NaHCO₃ was added and the resulting mixtures were concentrated in vacuo to give residues which were dissolved in CH2Cl2 and washed with water. The organic layers were dried over Na₂SO₄ and concentrated *in vacuo* to yield crude product mixtures which were subjected to ¹H NMR analysis and chromatographic separation.

Irradiation of Iminium Perchlorate (**7**). ¹H NMR analysis of the crude photolysate showed that it contained a mixture of enaminone **23** and other unidentified substances. None of the spectral characteristics of the spirocyclic amine **34** was observed.

Irradiation of Iminium Perchlorate (**8**). Iminium salt **8** in CH₃CN (69 mg, 0.11 mmol in 117 mL) was irradiated until the absorbance at 287 nm was 49% of the initial value. Work-up followed by chromatography on F-20 alumina

gave 10 mg (21%) of spirocyclic amine **35** (elution with CHCl3) and 19 mg (41%) of enaminone **27** (elution with ethyl acetate). **35**: UV max (CH₃CN) 290 nm (ε 3100); ¹H NMR 1.00 (s, 9 H, C(CH₃)₃), 1.58 (ddd, J=13.5, 9.7, 8.2 Hz, 1 H, H-9), 2.12 (d J=15.5 Hz, 1 H, H-4), 2.20-2.40 (m, 3 H, H-9, H-8, H-4), 2.41 (s, 3 H, NCH₃), 2.56-2.86 (m, 3H, H-8, ArCH₂), 3.04 (dd, J=14.0, 2.4 Hz, 1 H, H-2), 3.34 (s, 3H, OCH₃), 3.44, 3.49 (overlapping t, J=6.7 Hz, 2 H, CH₂O), 3.57 (d, J=14.0 Hz, 1 H, H-2), 4.77 (br s, 2 H, C=CH₂), 5.85, 5.88 (ABq, J=1.4 Hz, 2 H, OCH₂O), 6.69 (s, 1 H, ArH), 6.70 (s, 1 H, ArH); ¹³C NMR (CD₃CN), 26.3 (C-9), 27.2 (C(CH₃)₃), 31.0 (C-8), 34.0 (ArCH₂), 34.3 (NCH₃), 39.6 (C(CH₃)₃), 45.4 (C-4), 58.4 (C-2), 58.7 (OCH₃), 73.9 (CH₂O), 77.1 (C-5), 102.2 (OCH₂O), 105.2 (C=CH₂), 109.8 (C-3'), 110.6 (C-6'), 126.6 (C-1'), 127.1 (C-6), 133.2 (C-2'), 146.3 (C-3), 147.9 (C-4'), 148.1 (C-5'), 151.7 (C-7), 176.7 (O=C-O); IR (CHCl₃) 2920, 2860, 1735, 1675 (w), 1480, 1365, 1275, 1135, 1110, 1040, 940, 880, 860; MS m/z (rel intens) 427 (M, 30), 396 (10), 370 (15), 342 (45), 326 (25), 310 (20), 294 (12), 280 (25), 185 (15), 167 (25), 149 (95), 122 (30), 108 (100); HRMS m/z 427.2356 (C₂₄H₃₃NO₅ requires 427.2359).

Irradiation of Iminium Perchlorate (**9**). Iminium salt **9** in CH₃CN (661 mg, 0.977 mmol in 330 mL) was irradiated until the absorbance at 285 nm was 46% of the initial value. Work-up followed by F-20 alumina column chromatography gave 244 mg (45%) of spirocyclic amine **36** (elution with 90:10 hexanes/ethyl acetate) and 138 mg (29%) of enaminone **29** (elution with ethyl acetate). **36** UV max (CH₃CN) 291 nm (ε 4000); ¹H NMR 1.00 (s, 9 H, C(CH₃)₃), 1.71 (ddd, J=13.7, 9.8, 8.2 Hz, 1 H, H-9), 2.20 (d, J=15.3 Hz, 1 H, H-4), 2.39 (overlapping ddd, J=13.7, 8.6, 7.4 Hz, 1 H, H-9), 2.41 (overlapping ddd, J=16.5, 9.8, 8.6 Hz, 1 H, H-8), 2.51 (dd, J=15.3, 2.2 Hz, 1 H, H-4), 2.69-2.84 (m, 3 H, H-8, ArCH₂), 2.89 (dd, J=14.2, 2.2 Hz, 1 H, H-2), 3.27 (d, J=13.6 Hz, 1 H, ArCH₂N), 3.37 (s, 3 H, OCH₃), 3.47 (overlapping d, J=14.2 Hz, 1 H, H-2), 3.48 (overlapping dt, J=9.0, 6.2 Hz, 1 H, CH₂O), 3.55 (dt, J=9.0, 6.2 Hz, 1 H, CH₂O), 4.52 (d, J=13.6 Hz, 1 H, ArCH₂N), 4.73, 4.78 (s and s, 2 H, C=CH₂), 5.87, 5.88 (ABq, J=1.4 Hz, 2 H, OCH₂O), 6.75 (s, 1 H, ArH), 6.77 (s, 1 H, ArH), 7.19-7.41 (m, 5 H, benzyl group ArH); ¹³C NMR (CD₃CN) 27.2 (C(CH₃)₃), 27.3 (C-9), 31.0 (C-8), 34.0 (ArCH₂), 39.6 (C(CH₃)₃), 45.2 (C-4), 52.6 (C-2), 55.8 (ArCH₂N), 58.7 (OCH₃), 73.9 (CH₂O), 77.6 (C-5), 102.2 (OCH₂O), 105.7 (C=CH₂), 109.9 (C-3'), 111.0 (C-6'), 126.4 (C-1'), 127.5 (C-6), 127.7, 129.1, 129.4 (benzyl group C-H aromatic), 133.2 (C-2'), 141.0 (benzyl group C-1 aromatic), 146.3 (C-3), 147.5 (C-4'), 148.0 (C-5'), 152.4 (C-7), 176.7 (O=C-O); IR (CHCl₃) 2920, 1740, 1675 (w), 1480, 1450, 1365, 1320, 1275, 1230, 1170, 1130, 1105, 1040, 965, 940, 885, 865; MS m/z (rel intens) 503 (M, 8), 446 (5), 418 (17), 402 (8), 356 (4), 312 (5), 252 (5), 184 (26), 149 (5), 135 (6), 106 (19), 91 (91), 86 (45), 84 (73), 77 (13), 57 (100); HRMS m/z 503.2647 (C₃₁H₃₇NO₅ requires 503.2672).

Irradiation of Iminium Perchlorate (**10**). ¹H NMR analysis of the crude photolysate showed that it contained a mixture of enaminone **28** and other unidentified substances. None of the spectral characteristics of the desired spirocyclic amine was observed.

Irradiation of Iminium Perchlorate (**11**). Irradiation of iminium salt **11** in CH₃CN (41 mg, 0.066 mmol in 112 mL) was conducted until the absorbance at 287 nm was 48% of the initial value. Work-up followed by F-20 alumina column chromatography gave 5 mg (17%) of spirocyclic amine **37** (elution with 90:10 hexanes/ethyl acetate) and 15 mg (52%) of enaminone **30** (elution with ethyl acetate). **37** UV max (CH₃CN) 293 nm (ε 4600), 259 nm (ε 5700); ¹H NMR 1.17 (s, 9 H, C(CH₃)₃), 1.66 (ddd, J=13.5, 9.7, 7.3 Hz, 1 H, H-9), 2.21 (d, J=15.7 Hz, 1 H, H-4), 2.32 (ddd, J=13.5, 8.9, 2.7 Hz, 1 H, H-9), 2.48 (ddd, J=16.5, 9.7, 2.7 Hz, 1 H, H-8), 2.68 (ddd (7 lines), J=16.5, 8.9, 7.3 Hz, 1 H, H-8), 2.85 (dd, J=15.7, 2.1 Hz, 1 H, H-4), 2.95 (dd, J=14.1, 2.1 Hz, 1 H, H-2), 3.21 (d, J=12.9 Hz, 1 H, ArCH₂N), 3.46 (d, J=14.1 Hz, 1 H, H-2), 4.23 (d, J=12.9 Hz, 1 H, ArCH₂N), 4.78, 4.81 (s and s, 2 H, C=CH₂), 5.92 (s, 2 H, OCH₂O), 6.76 (d, J=8.1 Hz, 1 H, H-5'), 7.13 (dd, J=8.1, 1.6 Hz, 1 H, H-6'), 7.17-7.34 (m, 6 H, H-2' and benzyl group ArH); ¹³C NMR 26.1 (C-9), 27.0 (C(CH₃)₃), 29.9 (C-8), 38.9 (C(CH₃)₃), 44.5 (C-4), 52.4 (C-2), 55.0 (ArCH₂N), 76.4 (C-5), 100.8 (OCH₂O), 105.1 (C=CH₂), 107.7 (C-5'), 109.4 (C-2'), 122.6 (C-6'), 126.3 (C-1'), 126.6 (benzyl group C-H aromatic), 127.2 (C-6), 128.2, 128.6 (benzyl group C-H aromatic), 139.8 (benzyl group C-1 aromatic), 146.4 (C-3), 146.5 (C-4'), 147.1 (C-3'), 149.8 (C-7), 175.9 (O=C-O); IR (CHCl₃) 3020, 2965, 2930, 1735, 1650 (w), 1500, 1480, 1450, 1225, 1140, 1120, 1050, 930; MS m/z (rel intens) 445 (M, 60), 360 (50), 344 (25), 306 (19), 269 (7), 212 (6), 198 (6), 184 (18), 149 (12), 91 (100), 57 (97); HRMS m/z 445.2238 (C₂₇H₃₃NO₄ requires 445.2253).

Irradiation of Iminium Perchlorate (**12**). ¹H NMR analysis of the crude photolysate showed that it contained a mixture of enaminone **26** and other unidentified substances. None of the spectral characteristics of the desired spirocyclic amine was observed.

RESULTS AND DISCUSSION

Synthetic Issues.

The first issue addressed in this study was the synthesis of the iminium salts **7-12**. Our earlier studies[8,9] guided the selection of β-enamino ketones as reasonable precursors to these substances. Accordingly, the methoxyethyl side chain containing salts **7-9** are prepared from the enamino ketone **23** by sequential N-alkylation and O-acylation. Preparation of **23** follows a sequence (Scheme 3) which takes advantage of Semmelhack's methodology[10] to construct the piperonyl alcohol **17** from commercially available piperonal (**13**), a Janssen-Wilson protocol[11] for aryl iodide **19** formation, halogen metal interchange for carboxaldehyde production, the Kuwajima procedure[12] for 2-arylcyclopentane dione **22** synthesis, an adaptation of the Rapoport method[13] to vinylogous acid chloride generation, and final vinylogous amide formation by reaction of **22** with 2-(trimethylsilylmethyl)-3-propenyl amine. A related

route (Scheme 4), starting with piperonal, was employed to prepare the non-side chain containing enaminone **26**, the precursor of iminium salts **10-12**.

The β-enaminone **23** is directly converted to the silylallyl-iminium perchlorate **7** by treatment with pivaloyl chloride and silver perchlorate (Scheme 5). The N-methyl and N-benzyl derivatives **8** and **9** are
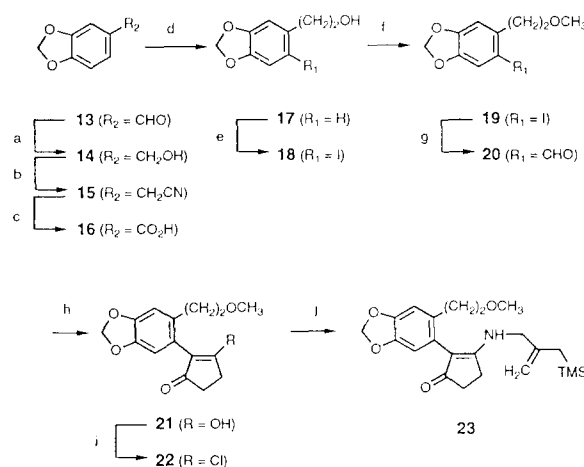
Scheme 3. Reagents and conditions are as follows: (a) NaBH₄, EtOH, 97%; (b) conc. HCl; NaCN, NaI, acetone, 89%; (c) KOH, EtOH-H₂O, 91%; (d) LiAlH₄, THF, 90%; (e) I₂, AgO₂CCF₃, 83%; (f) CH₃I, NaOH, 97%; (g) n-BuLi, N-formylpiperidine, 82%; (h) 1,2-bis(trimethylsiloxy)cyclobutene, BF₃-OEt₂, CH₂Cl₂, -78°C; CF₃CO₂H, 0°C, 75%; (i) NaOH, ClCOCOCl, 99%; (j) H₂NCH₂(TMSCH₂)C=CH₂, K₂CO₃, 82%.
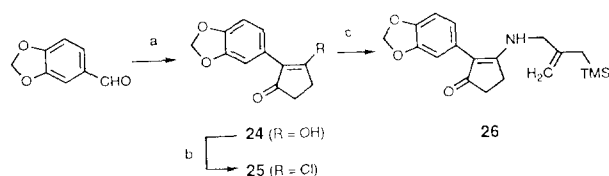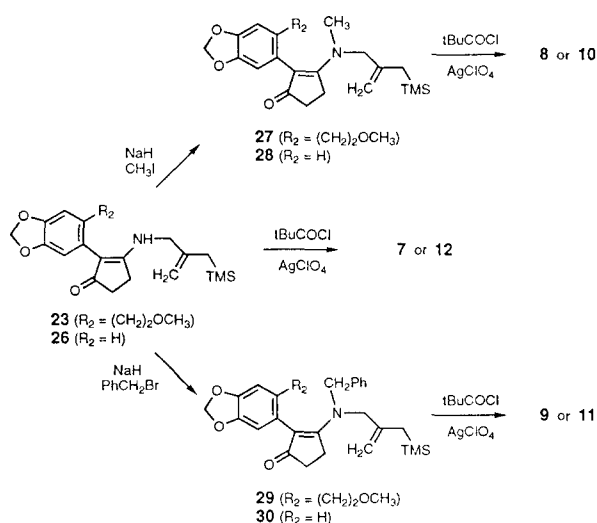
Scheme 4. Reagents and conditions are as follows: (a) 1,2-bis(trimethylsiloxy)-cyclobutene, BF₃-OEt₂, CH₂Cl₂, -78°C; CF₃CO₂H, 0°C, 68%; (b) NaOH, ClCOCOCl, 100%; (c) H₂NCH₂(TMSCH₂)C=CH₂, K₂CO₃, 86%.

prepared from **23** by respective N-methylation and benzylation and independent O-pivaloylation of the derived tertiary enaminones **27** and **29**. Likewise, the iminium salts **12**, **10**, and **11** are generated from the enaminones **26**, **28** and **30**, respectively.

Structural Issues.

As mentioned above, the aryliminium salts **7-12**, which in most cases are mixtures of E and Z C=N isomers, can exist in either preferential planar (conjugated) or non-planar (non-conjugated)

27 (R$_2$ = (CH$_2$)$_2$OCH$_3$)
28 (R$_2$ = H)

NaH
CH$_3$I

iBuCOCl
AgClO$_4$ **8 or 10**

23 (R$_2$ = (CH$_2$)$_2$OCH$_3$)
26 (R$_2$ = H)

iBuCOCl
AgClO$_4$ **7 or 12**

NaH
PhCH$_2$Br

iBuCOCl
AgClO$_4$ **9 or 11**

29 (R$_2$ = (CH$_2$)$_2$OCH$_3$)
30 (R$_2$ = H)

Scheme 5.

conformations depending on the competitive effects of electronic stabilization through conjugation and of biphenyl-like steric destabilization. Qualitative information about the conformational preferences in these systems can be gained by inspection of their UVspectroscopic and ^{1}H NMR spectroscopic properties. For example, for those iminium salts which exist in planar conformations (*e.g.* **31**), their dioxolene A-ring methylene protons are enantiotopic and, thus, resonate as 2H singlets in the ^{1}H NMR spectrum. In contrast, the existence of a non-planar conformation introduces a center of chirality into the iminium salt, making the A-ring methylene protons diastereotopic and, thus, their appearance as an AB-quartet in the ^{1}H NMR. In addition, the UV spectroscopic properties of aryl-iminium salts which exist in non-planar conformations should reflect their non-aryl-conjugated nature and, as a results, they should mimic those of simple non-aryl analogs. As can be seen by viewing the data given in Table 1, the wavelength maxima of the methoxyethyl side chain bearing iminium salts **7-9** all occur between 277-287 nm and match those of their non-aryl analogs **32** and **33**.[8,9] This is also true for the N-benzyl non-side chain derivative **11**. In addition, analysis of the ^{1}H NMR spectra of **7-9** and **11** demonstrates that these substances contain diastereotopic dioxolene-ring methylene protons. Thus, it is reasonable to conclude that in these salt, steric interactions outweigh electronic stabilization and cause preferences for non-planar conformations.

In contrast, the non-side chain containing N-H iminium salt **12** has UV-properties that match those of the tetracyclic analog **31**[8] and its methylene protons resonate as a singlet. Owing to reduced steric

repulsion, this substance appears to exist in a planar conformation. Finally, the situation with the N-CH$_3$ relative is more complicated in that its UV and ^{1}H NMR properties are more consistent with its existence as a mixture of planar and non-planar conformers.

With iminium salts **7-12** prepared and information

Table 1. UV and ^{1}H NMR Characteristics of Aryl-Iminium Salts **7-12** and Related Substances **31-33**.
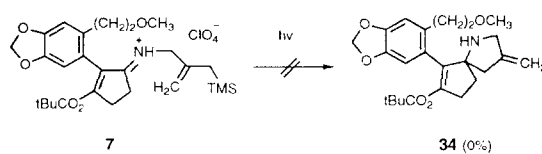
Iminium Salt	λ_{max} (nm, MeCN)	Dioxolene ^{1}H NMR Resonance	Conformational Preferences
31	290, 315 (s)	singlet	planar
32	265	–	–
33	273	–	–
7	277	AB-quart.	non-planar
8	287	AB-quart.	non-planar
9	285	AB-quart.	non-planar
10	278, 320 (s)	AB-quart.	none
11	287	AB-quart.	non-planar
12	269, 320 (s)	singlet	planar

31

32 (R = H)
33 (R = CH$_3$)
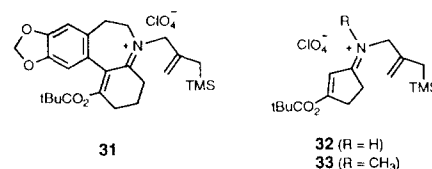
Structures 31-33
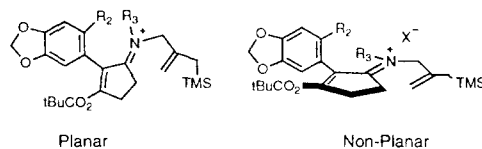
Planar   Non-Planar

Structures Planar and Non-Planar

**7**   **34** (0%)

Structures 7-34

about their conformational preferences gathered, attention then turned to the photochemical reactivity of these substances. The photochemistry of the

methoxyethyl substituted N-H salt **7** was explored first. A solution of **7** in MeCN was irradiated in a preparative apparatus by using Corex filtered-light (λ > 280 nm). Reaction was allowed to proceed to *ca.* 50% conversion of **7** as judged by UV monitoring of removed aliquots. Basic work-up of the concentrated photolysate led to a product mixture which by ¹H NMR analysis was shown to contain the enaminone **23** predominantly. Importantly, this analysis failed to reveal the presence of spirocyclic-amine **34** in this mixture. Attempts to promote photoconversion of **7** to **34** by use of added perchloric acid, of the more polar-nucleophilic solvent MeOH, or of xanthone triplet sensitization all met with failure.

In contrast to this, the N-CH₃ iminium perchlorate **8** is observed to undergo photocyclization to produce the spirocyclic-amine **35**. Irradiation of an MeCN solution of **8** with Corex filtered-light led to a steady decrease in the UV-absorption maximum of **8** at 287 nm with isosbestic points established at 240 and 310 nm. Irradiation was stopped when the absorbance at

8 (R₃ = CH₃)
9 (R₁ = PhCH₂)

35 (R₃ = CH₃) (42%)
36 (R₃ = PhCH₂) (98%)
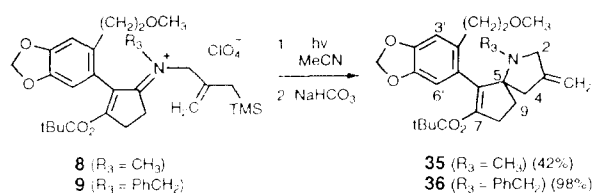
Structures 8-36

287 nm decreased by *ca.* 50% and the crude photolysate was then subjected to basic work-up and alumina chromatography. This procedure yielded the spirocyclic-amine **35** (21%, 42% based on 50% conversion of **8**) and the b-enaminone **27**.

The structure of **35** was assigned on the basis of characteristic spectroscopic properties. Notable in this regard is the ¹H NMR spectrum of this substance which contains a 9H singlet at 1.0 ppm for the pivaloyl methyls, doublets at 2.1 and 2.4 ppm for the pyrrolidine ring H-4 protons and at 3.0 and 3.6 ppm for the pyrrolidine H-2 protons, a broad singlet at 4.77 ppm for the exocyclic methylene hydrogens, and an AB-quartet at 5.85 and 5.88 ppm for the diastereotopic dioxolene A-ring protons.

An aspect of this photoreaction that has synthetic implications concerns secondary reactions of the initially formed photoproduct. Firstly, a dark control reaction of **8** followed by basic work-up afforded the enaminone **27** quantitatively. This demonstrates that **27** arises by reaction of **8** with base during work-up. Secondly, extended irradiation leading to 75% conversion of **8** followed by basic work-up and chromatographic separation gave **35** in a 20% yield

and enaminone **27** in only an 18% yield. This observation suggests that at high conversion, the photoproduct **35** undergoes secondary (unidentified) photoreaction(s), an unavoidable event owing to its .5UV-absorption properties (λ_max = 290, ε = 3,100). This limitation (*i.e.*, the need to conduct low conversion irradiations in order to obtain higher yield), although generally the case for the aryl-substituted iminium salt photoreactions probed in this study, is not as severe as might be anticipated since unreacted iminium salts such as **8** are converted to enaminone such as **27** upon basic work-up and the enaminone can be recycled to produce starting iminium salts in near quantitative yield by the one-step O-pivaloylation procedure.

The methodology established for photoreaction of the N-CH₃ iminium salt are applicable to promoting conversion of the N-benzyl analog **9** to the spirocyclic-amine **36**. Accordingly, irradiation of **9** in MeCN for a time period required to bring about 46% conversion followed by basic work-up and chromatographic separation led to isolation of **36** (45%, 98% based on 46% conversion) and the enaminone **29** (29%).

Clearly, the efficiencies of the SET-promoted photocyclization reactions of the side chain containing aryliminium salts **7-9** are highly dependent upon the nature of the N-substituents. With this result in mind, we next explored the photochemical properties of the iminium salts **10-12** which lack the ortho-disposed aryl ring side chain. Independent irradiations of MeCN solutions of the N-H and N-CH₃

11

37 (68%)
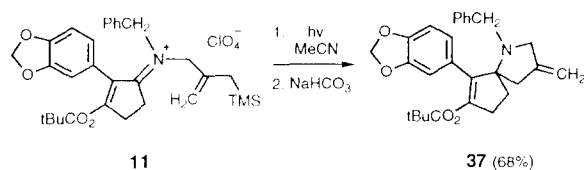
Structures 11-37

salts **10** and **12** failed to produce any of the corresponding spirocyclic-amine products. However, the N-benzyl derivative **11**, upon irradiation (50% conversion) in MeCN followed by basic work-up and alumina chromatography, is transformed to the spirocyclic-amine **37** (34%, 68% at 50% conversion).

Interpretive Discussion.

An initial goal of this investigation was to ascertain the relationship between structural features of the aryl-iminium salts and the efficiency of their SET-photoinduced spirocyclization processes. As can be seen by reviewing the results presented above, the

aryl side chain containing N-methyl and N-benzyl iminium salts **8** and **9** participate in the photoinduced spirocyclic-amine forming process with the efficiency of the latter process being excellent (Table 2). In contrast, the N-H analog **7** is unreactive in this manner. Also, the only aryl-iminium salt lacking the ortho side chain which undergoes photocyclization is the N-benzyl derivative **11** and here the efficiency is only moderate.

Table 2. Summary of the Results of Photoreactions of Aryl-Iminium Salts **7-12**.

Iminium Salt	Ortho-Aryl Side Chain	N-Substituent	Yield Spirocyclic Amine
7	$CH_2CH_2OCH_3$	H	0%
8	$CH_2CH_2OCH_3$	CH_3	42%
9	$CH_2CH_2OCH_3$	$PhCH_2$	98%
10	H	CH_3	0%
11	H	$PhCH_2$	68%
12	H	H	0%

When these results are placed in the context of the structural information provided in Table 1 and intuition about the effect of side-chain and nitrogen substituent on aryl-iminium ring conformations is applied, a uniform trend becomes apparent in the photoreactivity of **7-12**. In general, it appears that the efficiencies for SET-induced excited state reactions of these substances is related to the extent to which they exist in non-planar ground state conformations. For example, salt **12**, whose NMR and UV properties suggest exists in a planar conformation, is unreactive toward photocyclization. Moreover, even though the same data for **7** and **10** suggest that non-planar ground state structures are preferred for the most part, the lack of large nitrogen or side chain substituents in these substances might be responsible for a significant degree of orbital overlap between the electron rich aryl and iminium salt chromophores. As we have shown earlier, this feature leads to suppression of SET-reactivity by governing the excited state reduction potential of the iminium cation grouping. Finally, in the two cases where a bulky N-benzyl group is present, *i.e.* **9** and **11**, and as a result a non-planar conformation would be enforced, photocyclization reaction efficiencies are high.

CONCLUSION

This investigation has led to the development of new methods to prepare structurally complex aryl-iminium salts. Moreover, it has shown that SET-promoted photoreactions of these substances, which contain allylsilane functions as tethered donors, can occur efficiently to produce spirocyclic-amine products. The efficiencies of these photoprocesses and their dependence on aryl ring ortho and nitrogen substituents appear to correlate with structural features which govern their existence in either non-planar (reactive) or planar (unreactive) conformations.

REFERENCES

1. Mariano, P. S. (1983) Electron Transfer Mechanisms in Photochemical Transformations of Iminium Salts. *Acc. Chem. Res.* **16**, 130-137.
2. Mariano, P. S. (1987) The Photochemistry of Substances Containing th C=N Moiety with Emphasis on Electron Transfer Processes. In *Organic Photochemistry*; Padwa, A., Ed., *Vol.* **9**, 1-128. Marcel Dekker, New York.
3. Mariano, P. S. and J. L. Stavinoha (1983) Synthetic Aspects of Photochemical Electron Transfer Reactions. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed., 145-257. Plenum, New York.
4. Cho, I-S., C. -L. Tu and P. S. Mariano (1990) Electron Transfer Induced Photochemical Reactions of Sillylallyl-Iminium and Benzylpyrrolin-iumSalts by Dual Diradical and Diradical Cation Cyclization Pathways. *J. Am. Chem. Soc.* **112**, 3594-3607.
5. Ho, G. C. and P. S. Mariano (1988) Exploratory, Mechanistic and Synthetic Aspects of Slylarene-Iminium Salt SET Photochemistry. Studies of Diradical Cyclization Processes and Applications to Protoberberine Alkaloid Synthesis. *J. Org. Chem.* **53**, 5113-5127.
6. Ahmed-Schofield, R. and P. S. Mariano (1987) A Photochemical Route for Erythrinane Ring Construction. *J. Org. Chem.* **52**, 1478-1482.
7. Hudkicky, T, L. D. Kwart and J. W. Reed (1987) Synthesis of Cephalotaxine Alkaloids Alkalois. In *Chemical and Biological Perspectives*, Pelletier, S. W. Ed., Vol. 5, 639-691. .Springer-Verlag, New York
8. Ullrich, J. W., F. -T. Chiu, T. Tiner-Harding and P. S. Mariano (1984) Electron Transfer Initiated Photospirocyclization Reactions of β-Enaminone Derived Allyl-Iminium Salts. *J. Org. Chem.* **49**, 220-228.
9. Chiu, F.-T., J. W. Ullrich and P. S. Mariano (1984) Model Studies Examining the Application of Allyl-Iminium Salt Photospirocyclization Methodologies in Synthetic Approaches to the Harringtonine Alkaloids. *J. Org. Chem.* **49**, 228-236.

10. Semmelhack, M. F., B. P. Chong, R. D. Stauffer, T. D. Rogerson, A. Chong and L. D. Jones (1975) Total Synthesis of the Cephalotaxus Alkaloids. A Problem in Nucleophilic Aromatic Substitution. *J. Am. Chem. Soc.* **97**, 2507-2516.

11. Janssen, D. E. and C. V. Wilson (1963) 4-Iodoveratrole. *Org. Syn., Coll.* **4**, 547-549.

12. Shimada, J., K. Hashimoto, B. H. Kim, E. Nakamura and I. Kuwajima (1984) Ring Expansion and Cleavage of Succinoin Derivatives.Geminal Acylation, Reductive Succinoylation and Stereoselective Spiro-Annelation Methods. *J. Am. Chem. Soc.* **106**, 1759-1773.

13. Rapoport, H. and C. D. Willson (1962) Preparation and Properties of Some Methoxypyrroles. *J. Am. Chem. Soc.* **84**, 630-635.

14. Shepard, E. R., H. D. Porter, J. F. Noth and C. K. Simmons (1952) Preparation of Some Analogs of Papaverine. *J. Org. Chem.* **17**, 568-576.

15. Lindley, J. (1984) Copper Assisted Nucleophilic Substitution of Aryl Halogen. *Tetrahedron* **40**, 1433-1456.